Photooxidation of 1,1,1-Trimethyl-2,2,2-triphenyldisilane by Dimethyl Sulfoxide

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Abstract: Photooxidation of 1,1,1-trimethyl-2,2,2-triphenyldisilane (I) by Me$_2$SO in a variety of ether solvents is found to yield dimethyl sulfide, 1,1,1-trimethyl-3,3,3-triphenyldisiloxane (II), phenyltrimethylsilane (III), octaphenylcyclotetrasiloxane (IV), and a small amount of triphenylmethylsilane (V). The yields of III and IV are approximately equal. The ratio of products II to III is highly dependent on the specific ether solvent. The intermediacy of diphenylsilanone [ϕ_2Si=O] has been demonstrated by trapping experiments. Quantum yields for the disappearance of I and the appearance of II and III have been measured. The dependence of the quantum yield for the disappearance of Me$_2$SO on the concentration of Me$_2$SO has been determined. These results have been interpreted in terms of competition between reaction of the photoexcited state of I with Me$_2$SO, its direct decomposition, and its deactivation.

We have been interested in the photochemical generation and subsequent chemistry of silanone intermediates, reactive species possessing a formal silicon–oxygen double bond [R$_2$Si=O].[1-4] In this connection, we should like to report our results on the photolysis of 1,1,1-trimethyl-2,2,2-triphenyldisilane (I) in the presence of dimethyl sulfoxide (Me$_2$SO) at 25 °C in various ether solvents by using monochromatic (2537 Å) light which provides an efficient route to diphenylsilanone [ϕ_2Si=O]. Photochemical reaction of I under these conditions occurs by three competing pathways in which oxygen is transferred from Me$_2$SO to silicon with concurrent formation of dimethyl sulfide (Me$_2$S).

The first pathway involves oxidation of I by Me$_2$SO to yield 1,1,1-trimethyl-3,3,3-triphenyldisiloxane (II) and an equal


$$\longrightarrow \quad (CH_3)_3Si\text{-}O\text{-}SiPh_3 + Me_2S$$
$$\text{II}$$
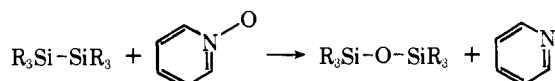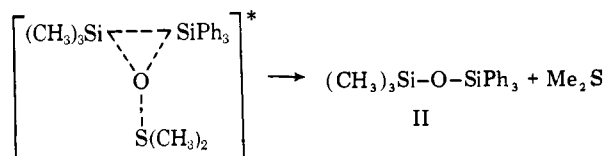
amount of Me$_2$S. This may result from nucleophilic attack by the oxygen of Me$_2$SO on the photoexcited Si–Si single bond of I. While this photooxidation of I may be related to the thermal oxidation of disilane to disiloxane by peroxy acids,[5-7] oxides of nitrogen,[8] and pyridine N-oxides,[9] control experiments have shown that I is not oxidized to II by Me$_2$SO under vigorous thermal conditions (heating at 100 °C for 18 h).

The other two photooxidation pathways may be related. In one, nucleophilic attack of the oxygen of Me$_2$SO on the triphenylsilyl center of the photoexcited disilane causes a phenyl group to migrate to the trimethylsilyl center resulting in formation of phenyltrimethylsilane (III), diphenylsilanone, and Me$_2$S in a single step. In the absence of trapping reagents, diphenylsilanone undergoes cyclooligomerization to give octaphenylcyclotetrasiloxane (IV). Consistent with the above equations, the yields of III and IV are approximately equal (see Table I). Diphenylsilanone has been efficiently trapped by insertion into silicon–oxygen single bonds. Reactions carried out in dimethoxydimethylsilane and hexamethyldisiloxane as solvents yield respectively 1,3-dimethoxy-1,1-dimethyl-3,3-diphenyldisiloxane (83%) and 1,1,1,5,5,5-hexamethyl-3,3-diphenyltrisiloxane (50%). Yields are calculated based on the amount of III which should be equal to the diphenylsilanone generated. Thus, diphenylsilanone is trapped quite efficiently by both Si–O–C and Si–O–Si single bonds. The only previous

$$\longrightarrow [Ph_2Si=O] + Me_2S + (CH_3)_3SiPh$$
$$\text{III}$$

$$[Ph_2Si=O] \longrightarrow$$
$$\text{IV}$$
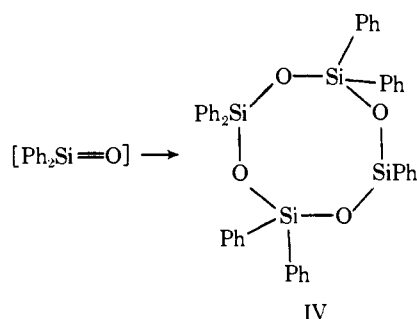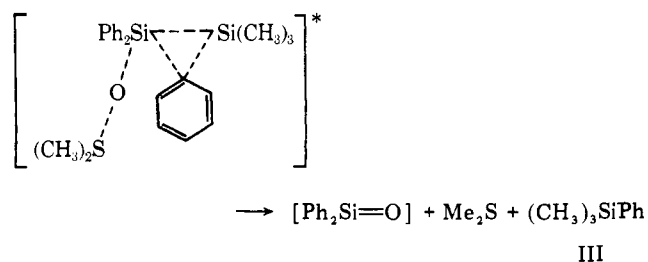
report of diphenylsilanone involves formation of this intermediate in a gas-phase copyrolysis reaction of 1,1-diphenylsilacyclobutane and heptanal at 611 °C.[10] Certainly, the photochemical oxidation process here reported provides an efficient method to generate this species in solution.

The other pathway may occur by nucleophilic attack of the oxygen of Me$_2$SO on the trimethylsilyl center of the photoexcited disilane. This causes a methyl group to migrate to the triphenylsilyl center resulting in formation of methyltriphenylsilane (V), Me$_2$S, and dimethylsilanone[11] in a single

$$\longrightarrow Me_2S + [(CH_3)_2Si=O] + CH_3SiPh_3$$
$$\text{V}$$
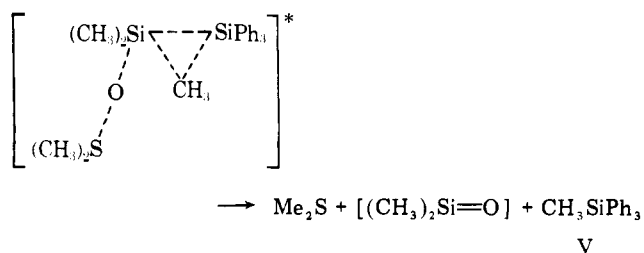
step. Phenyl migration occurs much more readily than methyl migration, since the yield of III is about ten times that of V in a variety of ether solvents.

The following data support the proposed mechanisms. First, in the absence of Me$_2$SO, I is found to undergo photochemical decomposition to yield nonvolatile products. Second, control experiments have demonstrated the stability of the products

Table I. Products from Photolysis of I in Ether Solvent with Me$_2$SO

solvent	Ph$_3$Si-O-Si-(CH$_3$)$_3$ II	PhSi-(CH$_3$)$_3$ III	[Ph$_2$Si-O]$_4$ IV	Ph$_3$Si-CH$_3$ V
tetrahydrofuran	72	22	21	1
p-dioxane	51	43	41	1.7
Et$_2$O	41	59		
furan	32	67	64	1

Table II. Quantum Yield Data for I and Me$_2$SO^a

time, s	I, mmol	II, mmol	III, mmol
expt 1: 1 and Me$_2$SO, 1:1			
0.0	0.180	0.000	0.000
900.0	0.153	0.017	0.007
1200.0	0.150	0.021	0.007
1800.0	0.139	0.026	0.015
2400.0	0.118	0.035	0.017
2700.0		0.042	0.021
3600.0	0.092	0.058	0.029
expt 2: 1 and Me$_2$SO, 1:0.4			
0.0	0.181	0.005	0.000
900.0	0.159	0.009	0.015
1800.0	0.130	0.014	0.036
2500.0	0.108	0.015	0.051
2700.0	0.107	0.017	0.055

^{a} Experiment 1: volume of solution in the NMR tube is 2.01 mL; the flux is 4.71×10^{-8} einstein/s. Experiment 2: volume of solution in the NMR tube is 2.01 mL; the flux is 9.14×10^{-8} einstein/s.

II, III, IV, and V to the photolysis conditions. Third, while disilanes are known to form charge-transfer complexes with tetracyanoethylene (TCNE),[12-16] no detectable complex (by ultraviolet spectroscopy) is formed between I and Me$_2$SO. Thus, the photooxidation of I by Me$_2$SO involves initial photoexcitation of I and not photoexcitation of a ground state complex of I and Me$_2$SO. The fourth type of evidence is kinetic. The quantum yield for the disappearance of I (0.1 M) in the presence of Me$_2$SO (0.1 M) in furan as solvent was found to be 0.51 ± 0.05, Φ = d[I]/mol of photons absorbed. The quantum yields for the appearance of II and III were found to be 0.17 ± 0.02 and 0.33 ± 0.03, respectively. Quantum yields are dependent on Me$_2$SO concentration. Thus, the quantum yield for the disappearance of I (0.1 M) in the presence of Me$_2$SO (0.041 M) was found to be $\Phi = 0.31 \pm 0.03$. The quantum yield for the disappearance of Me$_2$SO was found to be $\Phi = 0.24 \pm 0.03$. The quantum yields for the appearance of II and III were found to be 0.05 ± 0.01 and 0.21 ± 0.02, respectively. The disappearance of n-butyrophenone ($\Phi = 0.33$) and the appearance of acetophenone ($\Phi = 0.24$) in methylcyclohexane solvent were determined at the same time and were used as the actinometers.[17] These values were determined by GLPC analysis of the photolysis solutions at various times (see Table II for supporting data). The disappearance of Me$_2$SO was followed by ^{1}H NMR at various times.

While considerable work has been done in the last 10 years on the photochemistry of organosilicon compounds, as far as we are aware, there have only been two previous photochemical reactions for which quantum yields have been determined: specifically, the mercury sensitized photolysis of silanes to yield disilanes[18] and, more recently, the vacuum ultraviolet photolysis of hexamethyldisiloxane.[19]
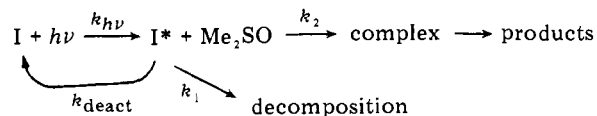
The rate of disappearance of Me$_2$SO was found to fit the kinetic expression given below (eq 1) which is derived on the assumption that a minute steady-state concentration of excited state I (I*) exists which is partitioned between deactivation

Table III. Stern–Volmer Relationship of I and Me$_2$SO in Furan^a

1/[Me$_2$SO]	1/Φ	symbol
run 1		
34.48	5.26	△
16.39	2.94	
run 2		
38.64	5.88	□
15.15	2.70	
10.53	1.92	
8.62	1.86	
run 3		
25.64	4.35	●
19.61	3.33	
13.70	2.44	
run 4		
47.62	6.67	▲
27.78	4.35	
24.39	4.00	
17.86	3.39	
run 5		
10.00	2.00	○
24.39	4.20	

^{a} Volume of solution in quartz NMR tube: 2.07 (run 1), 2.01 (run 2), 1.94 (run 3), 1.98 (run 4), and 2.01 mL (run 5).

to the ground state, decomposition, and efficient reaction with Me$_2$SO, possibly to form an excited complex which undergoes

$$I + h\nu \xrightarrow{k_{h\nu}} I^* + Me_2SO \xrightarrow{k_2} complex \longrightarrow products$$

$$\underbrace{}_{k_{deact}} \quad k_1 \searrow decomposition$$

further reaction to yield the products. The rate of disappearance of Me$_2$SO is equal to the rate of formation of the volatile products. On the basis of the proposed mechanism, $-d[Me_2SO]/dt = k_2[I^*][Me_2SO]$. Based on the steady-state approximation, the following expression may be written: $d[I^*]/dt = 0 = k_{h\nu}[I] - k_1[I^*] - k_{deact}[I^*] - k_2[I^*] \cdot [Me_2SO]$. At the concentrations of I used, all the incident light (2537 Å) is absorbed. Thus $k_{h\nu}[I]$ is a constant (I_a) equal to the flux. Therefore, $I_a = k_1[I^*] + k_{deact}[I^*] + k_2[I^*] \cdot [Me_2SO]$. The reciprocal of eq 1 is eq 2.

$$-d[Me_2SO]/dt = \frac{k_2 I_a[Me_2SO]}{k_1 + k_{deact} + k_2[Me_2SO]} \quad (1)$$

$$-dt/d[Me_2SO] = \frac{k_{deact} + k_1}{k_2 I_a[Me_2SO]} + \frac{1}{I_a} \quad (2)$$

On the basis of the above mechanism, the quantum yield for the disappearance of Me$_2$SO can be written as: $\Phi = k_2[Me_2SO][I^*]/I_a$. Recalling that $I_a = (k_1 + k_{deact} + k_2[Me_2SO])[I^*]$ at the limit of infinitely high Me$_2$SO concentration, the terms k_1 and k_{deact} will be small relative to $k_2[Me_2SO]$ and so, a Stern–Volmer plot of $1/\Phi$ vs. $1/[Me_2SO]$ should have one as an intercept.

We have measured the rates of disappearance of Me$_2$SO by ^{1}H NMR with cyclododecane as an internal standard for a variety of initial Me$_2$SO concentrations while holding the initial concentration of I constant (0.1 M). A plot of $1/\Phi$ vs. $1/[Me_2SO]$ is found to be linear. $1/\Phi = 0.13/[Me_2SO] + 0.88$. The intercept of this line is 0.88 which is close to the expected value of 1. (See Table III and Figure 1 for supporting data.)

If a diffusion-controlled reaction rate between the photoexcited disilane and Me$_2$SO is assumed, a lower limit on the lifetime of the excited disilane can be calculated, i.e., $k_2 = k_{diff}$.

In furan at 25 °C, η is 0.361.[20] The rate of diffusion can be calculated from the following equation: $k_{diff} = 8RT/3000\eta^{21}$ to equal 1.84×10^8 mol^{-1} s^{-1}. Since $(k_1 + k_{deact})/k_2$ has been determined from Figure 3 to be equal to 0.13, the value of k_1 + k_{deact} is 2.39×10^7 s^{-1}. The lifetime of I* can be calculated from $\tau = 1/(k_1 + d_{deact} + k_{diff}[Me_2SO])$. In the absence of Me_2SO, $\tau_0 = 1/(k_1 + k_{deact}) = 4.2 \times 10^{-8}$ s.

Finally, we would like to call attention to a most intriguing aspect of the photooxidation of I by Me_2SO. The ratio of the two major photochemical oxidation pathways is highly dependent on solvent. (See Table I for supporting data.) Clearly, furan is the best solvent if one wishes to maximize the formation of III and diphenylsilanone. Since photolysis of a ground-state complex has been ruled out, the effect of solvent on the product ratio cannot result from changes in solvation of a ground-state complex. Therefore, we would propose that the effect of solvent results from solvation of the excited complex formed between Me_2SO and I*. This solvation apparently affects the competition between the various pathways by which this complex breaks down to products.

Experimental Section

Samples were purified by preparative gas–liquid phase chromatography (GLPC) on a Gow-Mac 550 on a 40×0.25 in. 20% DCQF-1 on Chromosorb W 60–80 mesh column (A) or on a 40×0.25 in. 20% SE-30 on Chromosorb W 60–80 mesh column (B). Products yields were determined by GLPC by using cyclododecane as an internal standard and were corrected for sensitivity of the thermal conductivity detector to the various compounds. IR spectra of neat liquids were determined on KBr salt plates, while those of solids were run in KBr pellets by using a Perkin-Elmer 281. The spectra were calibrated against known bands in a polystyrene film. NMR samples were run in acetone-d_6 as 1% solution, and the spectra were recorded on a Varian XL-100 operating in the FT mode. UV spectra were determined in spectroquality cyclohexane on a Beckman Acta M spectrometer. High resolution mass spectra were determined on a Du Pont 21-492 at 70 eV ionizing voltage at the California Institute of Technology Analytical Laboratory, Pasadena, Calif. Low resolution mass spectra were performed on a Hewlett Packard 5992 B GC-MS by using a 36×0.25 in. 3% OV-1 column. Melting points were determined in capillaries by using a Hoover-Thomas melting point apparatus and are corrected.

Virtually all of the starting materials and products are known compounds. They were prepared following literature methods. Their physical and spectral properties are in full agreement with literature values. In those cases where complete spectral information has not been previously reported, we have included these data.

Ether Solvents. Tetrahydrofuran, diethyl ether, and p-dioxane were purified by distillation under nitrogen from the sodium ketyl of benzophenone immediately prior to use.

Furan was purified by distillation under nitrogen through a 50-cm vacuum jacketed Nicrome wire helical spiral column immediately prior to use.

Hexamethyldisiloxane (Silar) was purified by distillation as above, bp 98–99 °C lit. (bp 98.5 °C[22]).

Dimethoxydimethylsilane (Silar) was purified by distillation as above, bp 81–82 °C (lit. bp 81–82 °C[23]).

Dimethyl sulfoxide was distilled under reduced pressure from calcium hydride immediately prior to use, bp 70 °C/10 mm.

Cyclododecane was used as the internal standard for GLPC. It was dissolved in CH_2Cl_2 and purified by treatment with concentrated H_2SO_4 to remove olefinic impurities. The solution was then washed twice with a saturated aqueous solution of $NaHCO_3$ and then three times with water. The CH_2Cl_2 was removed by evaporation under reduced pressure. Final purification was by recrystallization from 95% ethanol, mp 60.5–61.5 °C (lit. mp 61–63 °C[24]).

1,1,1-Trimethyl-2,2,2-triphenyldisilane:[25-27] NMR δ 7.21 (s, 15 H), 0.16 (s, 9 H).

1,1,1-Trimethyl-3,3,3-triphenyldisiloxane:[5,28] UV λ 2710 Å (ϵ 747), 2650 (993), 2600 (952), and 2540 (836).

Phenyltrimethylsilane.[29]

Octaphenylcyclotetrasilasiloxane:[30,31] NMR δ 7.40–7.20 (m, 16 H), 7.16–6.84 (m, 24 H).

Triphenylmethylsilane:[31] UV λ 2700 Å (ϵ 642), 2660 (847), 2630
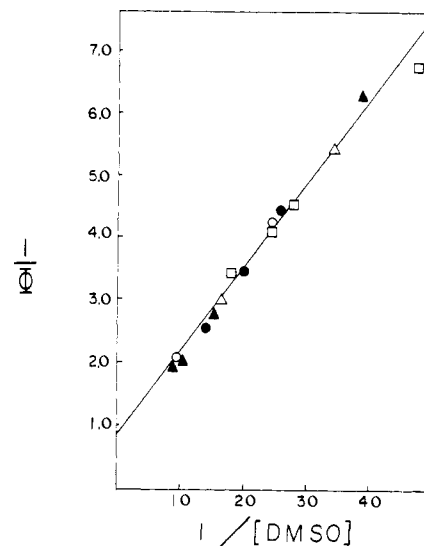

Figure 1. Stern–Volmer dependence on Me_2SO concentration of the quantum yield for reaction I with Me_2SO.

(904), 2590 (963), 2530 (699), 2470 (467); NMR δ 7.30 (m, 15 H), 0.60 (s, 3 H); mass spectrum molecular ion m/e 274 (26%), M $-$ 15 m/e 259 (100%).

1,1,1,5,5,5-Hexamethyl-3,3-diphenyltrisiloxane:[32] mass spectrum molecular ion m/e 360 (9%), M $-$ 15 m/e 345 (91%); NMR δ 7.34 (m, 10 H), 0.12 (s, 18 H).

1,3-Dimethoxy-1,1-dimethyl-3,3-diphenyldisiloxane: IR $SiPh_2$ 1115 cm^{-1} (d), Si-O and C-O 1070 and 1050 cm^{-1}; UV λ 2740 Å (ϵ 549), 2670 (726), 2620 (614), and 2560 (417); NMR δ 7.33 (m, 4 H), 7.13 (m, 6 H), 3.30 (s, 3 H), 3.15 (s, 3 H), $-$0.16 (s, 6 H); mass spectrum high resolution molecular ion m/e 318 (1%); Calcd for: $C_{16}H_{22}O_3Si_2$ 318.111. Found: 318.112. M $-$ 15 m/e 303 (37%). Calcd for $C_{15}H_{19}O_3Si_2$ 303.088. Found: 303.087.

Photolysis of 1,1,1-Trimethyl-2,2,2-triphenyldisilane (I) with Me_2SO. The following is a typical procedure. A mixture of I, 268 mg (0.8 mmol), Me_2SO, 62 mg (0.8 mmol), and cyclododecane, 67 mg (0.4 mmol), was dissolved in p-dioxane, 1.79 mL (20 mmol). The p-dioxane was deoxygenated by bubbling purified nitrogen through it for 15 min prior to making up the solution. The solution was placed in a 5.0-mm quartz tube. The tube was capped with a rubber septum. The tube was placed in a constant-temperature water bath which was maintained at 25 °C and was irradiated for 60 min with a 450-W medium pressure Hanovia Hg lamp. Similar results were obtained by irradiating the solution with monochromatic light at 2537 Å. For a description of this experimental procedure, see section entitled Quantum Yields. The amount of Me_2S was determined to be greater than 90% by NMR. GLPC analysis of the resulting yellow solution on column A showed the formation of II (51%), III (43%), V (1.7%), and IV (41%). The yields reported here are corrected for recovered starting material I (10%). The products II, III, IV, and V were purified by preparative GLPC on the same column after concentration of the photolysis solution by bulb-to-bulb distillation under reduced pressure (20 mm) to remove Me_2S and solvent. The products were identified by comparison of their IR and ^1H NMR spectra, GLPC retention times, and GC/MS with those of authentic samples.

Photolysis of Disilane (I) in the Absence of Me_2SO. A solution of I, 62 mg (0.187 mmol), in furan (2 mL) with cyclododecane, 13 mg (0.077 mmol), was photolyzed under the usual conditions for 100 min. Bulb-to-bulb distillation at 0.05 mmHg of the organic soluble products yielded 0.029 g of volatile material. GLPC on columns A and B showed this material to be unreacted I and cyclododecane. The non-volatile material and the increased weight of the quartz tube used in photolysis amounted to 0.046 g.

Quantum Yields. A stock solution of I, 0.33 g (1.0 mmol), Me_2SO, 0.078 g (1.0 mmol), and cyclododecane, 0.129 g (0.8 mmol), was made to 10 mL volume in furan. Equal amounts of this solution were transferred into 5-mm quartz NMR tubes. The tubes were sealed with rubber septums. The volume of the solution in the tubes was calculated from the height of solution in the tube and the tube's inner diameter. Simultaneous photolysis of a solution of 0.195 g of n-butyrophenone

and 0.092 g of cyclododecane (0.5 mmol) made to 5 mL volume with spectra quality methylcyclohexane in two 5-mm quartz NMR tubes of equal volume was used as actinometer. The photolysis was performed at the center of a circular (25.4-cm diameter) array of 16 equally spaced, 12-in. G.E. low-pressure mercury lamps. The sample tubes were immersed in a circulating water bath (25 °C). The bath was contained in a quartz sleeve (2.54-cm diameter) which was positioned at the center of the apparatus. Individual tubes were pulled from the reactor at various photolysis times for analysis. Multiple analyses of each tube by GLPC were carried out to establish the disappearance of I and *n*-butyrophenone and the appearance of II, III, and acetophenone. Two independent runs were performed and the data were normalized by comparison of the flux for each run. The average flux based on the disappearance of *n*-butyrophenone and the appearance of acetophenone was found to be 4.71×10^{-8} mol s^{-1} for the first run and 6.16×10^{-8} mol s^{-1} for the second run. See Table II.

The quantum yields for the disappearance of I and Me_2SO and the appearance of II and III were also determined with a stock solution of I 0.33 g (1.0 mmol), Me_2SO, 0.032 g (0.41 mmol), and cyclododecane, 0.129 g (0.8 mmol), made to 10-mL volume in furan. The quantum yield measurements were carried out as above with the exception that the concentration of Me_2SO was determined simultaneously at each interval by NMR integration vs. the internal standard of cyclododecane.

Stern–Volmer. A stock solution of I, 0.321 g (0.97 mmol), and cyclododecane, 0.0614 g (0.37 mmol), was made to 10 mL in furan. The solution was transferred into 5-mm quartz NMR tubes equipped with rubber septums. Me_2SO was added by microliter syringe. The Me_2SO concentration was determined by ^1H NMR integration relative to the cyclododecane internal standard prior to photolysis by using a Varian T-60 NMR spectrometer. The quantum yields at the different Me_2SO concentrations were determined by using a working curve established from the quantum disappearance of Me_2SO at 0.10, 0.04 M concentrations, and the expected intercept with Me_2SO present in a plot of $1/\Phi$ vs. $1/[Me_2SO]$. This line was used to determine the flux in independently run samples at Me_2SO concentrations below 0.1 M. The average flux for any one run was determined in this manner and the quantum yield was calculated from this information. See Table III and Figure 1.

Ground-State Complex. A solution of I, 0.044 g (0.13 mmol), was made to 10 mL volume in furan. UV spectra using matched 0.1-cm quartz cells were observed. Me_2SO was added to the solute and reference cells in 50 μL aliquots. No shift was noted in the UV spectrum of I above 2500 Å over the concentration range from 0 to 7×10^2 M equiv of Me_2SO.

Trapping with Hexamethyldisiloxane. A solution of I, 0.128 g (0.38 mmol), Me_2SO, 0.0297 g (0.38 mmol), and cyclododecane, 0.0766 g (0.046 mmol), was made to 2.5 mL volume in hexamethyldisiloxane. The solution was transferred into a 5-mm quartz NMR tube equipped with a rubber septum. GLPC analysis after photolysis showed II (31%), III (60%), IV (trace), and 1,1,1,5,5,5-hexamethyl-3,3-diphenyltrisiloxanes (30%). Yields are based on an 8% recovery of I.

Trapping with Dimethoxydimethylsilane. A solution of I, 0.1396 g (0.45 mmol), Me_2SO, 0.0352 g (0.45 mmol), and cyclododecane, 0.0752 g (0.45 mmol), was made to 2 mL in dimethoxydimethylsilane. The solution was transferred to a 5-mm quartz NMR tube equipped with a rubber septum. Analysis of the photolysis solution by GLPC showed II (33%), III (60%), IV (a trace), and 1,3-dimethoxy-1,1-dimethyl-3,3-diphenyldisiloxane (50%). Yields are based on a 33% recovery of I.

Photolysis Controls. A solution of III, 0.141 g (0.94 mmol), Me_2SO, 0.0737 g (0.94 mmol), and cyclododecane, 0.0592 g (0.35 mmol), was

made to 5 mL in furan. The solution was transferred to a 5-mm quartz tube. Integration of the ^1H NMR spectra before and after 20 min of photolysis at 25 °C showed no apparent loss of Me_2SO.

Similar experiments with II, IV, and V were conducted. ^1H NMR integration showed no loss of Me_2SO in any of these experiments.

Thermal Control. A solution of I, 0.1346 g (0.4 mmol), cyclododecane, 0.0536 g (0.3 mmol), and Me_2SO, 0.0320 g (0.4 mmol), was made to 5-mL volume in *p*-dioxane. The solution was placed in a 5-mm Pyrex NMR tube and freeze-thawed degassed through five cycles. The tube was sealed under 1 atm of nitrogen and heated for 18 h at 100 °C. There was no detectable change in the Me_2SO concentration by ^1H NMR integration. GLPC analysis showed no loss of I or formation of II.

References and Notes

(1) H. S. D. Soysa, H. Okinoshima, and W. P. Weber, *J. Organometal. Chem.*, **133**, C17 (1977).
(2) H. Okinoshima and W. P. Weber, *J. Organometal. Chem.*, **149**, 279 (1978).
(3) H. Okinoshima and W. P. Weber, *J. Organometal. Chem.*, **155**, 165 (1978).
(4) H. S. D. Soysa and W. P. Weber, *J. Organometal. Chem.*, in press.
(5) H. Sakurai, T. Imoto, N. Hayashi, and M. Kumada, *J. Am. Chem. Soc.*, **87**, 4001 (1965).
(6) H. Sakurai and Y. Kamiyama, *J. Am. Chem. Soc.*, **96**, 6192 (1974).
(7) K. Tamao, M. Kumada, and T. Takahashi, *J. Organometal. Chem.*, **94**, 367 (1975).
(8) L. Spialter and J. D. Austin, *J. Am. Chem. Soc.*, **88**, 1828 (1966).
(9) H. Sakurai, M. Kira, and M. Kumada, *Bull. Chem. Soc. Jpn.*, **44**, 1167 (1971).
(10) C. M. Golino, R. D. Bush, D. N. Roark, and L. H. Sommer, *J. Organometal. Chem.*, **66**, 29 (1974).
(11) Methyltriphenylsilane is produced in only about 1% yield. Dimethylsilanone will be formed only in this amount. The formation of dimethylsilanone has not been independently demonstrated by trapping experiments.
(12) V. F. Traven and R. West, *J. Am. Chem. Soc.*, **95**, 6824 (1973).
(13) H. Sakurai, M. Kira, and T. Uchida, *J. Am. Chem. Soc.*, **95**, 6826 (1973).
(14) M. Ishikawa, T. Fuchikami, and M. Kumada, *J. Organometal. Chem.*, **127**, 261 (1977).
(15) M. Ishikawa, T. Fuchikami, T. Sugaya, and M. Kumada, *J. Am. Chem. Soc.*, **97**, 5923 (1975).
(16) M. Ishikawa, T. Fuchikami, and M. Kumada, *J. Organometal. Chem.*, **118**, 139 (1976).
(17) R. D. Rauh and P. A. Leermakers, *J. Am. Chem. Soc.*, **90**, 2246 (1968).
(18) M. A. Nay, G. N. C. Woodall, O. P. Strausz, and H. E. Gunning, *J. Am. Chem. Soc.*, **87**, 179 (1965).
(19) H. P. Schuchmann, A. Ritter, and C. Von Sonntag, *J. Organometal. Chem.*, **148**, 213 (1978).
(20) J. A. Riddick and W. B. Bunger, "Organic Solvents, Physical Properties, and Methods of Purification", 3rd ed., Wiley-Interscience, New York, 1970, p 219.
(21) W. M. Horspool, "Aspects of Organic Photochemistry", Academic Press, New York, 1976, p 34.
(22) W. H. Daudt and J. F. Hyde, *J. Am. Chem. Soc.*, **74**, 386 (1952).
(23) D. Seyferth and E. G. Rochow, *J. Org. Chem.*, **23**, 250 (1955).
(24) L. Ruzicka, Pl. A. Plattner, and H. Wild, *Helv. Chim. Acta*, **29**, 1611 (1946).
(25) H. Gilman, D. J. Peterson, and D. Wittenberg, *Chem. Ind. (London)*, 1479 (1958).
(26) F. Hofler, *Monatsh. Chem.*, **107**, 893 (1976).
(27) H. Gilman, W. H. Atwell, and G. L. Schwebke, *J. Organometal. Chem.*, **2**, 369 (1964).
(28) J. Homer, A. W. Jarvie, A. Holt, and H. J. Hickton, *J. Chem. Soc. B*, 67 (1967).
(29) K. Bowden and E. A. Braude, *J. Chem. Soc.*, 1068 (1952).
(30) C. W. Young, P. C. Servais, C. C. Currie, and M. J. Hunter, *J. Am. Chem. Soc.*, **70**, 3758 (1948).
(31) E. W. Beck, W. H. Daudt, H. J. Fletcher, M. J. Hunter, and A. J. Berry, *J. Am. Chem. Soc.*, **81**, 1256 (1959).
(32) J. F. Brown, Jr., and P. I. Prescott, *J. Am. Chem. Soc.*, **86**, 1402 (1964).